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Rikard Källström. Corrosion during gasification of biomass and waste. Journal de Physique IV Proceedings, 1993, 03 (C9), pp.C9-751-C9-761. 10.1051/jp4:1993978 . jpa-00252420

HAL Id: jpa-00252420

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Submitted on 4 Feb 2008

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Corrosion during gasification of biomass and waste

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Abstract. — The gasification of biomass and waste results in severe atmospheric corrosion conditions. The problems arise because of the low oxygen content which prevents the metal forming stable and protective oxide surface layer. Consequently it is possible for the aggressive sulphur and chlorine present in the gas to attack the metal. In the Studsvik CFB gasification pilot plant, which uses RDF (Refuse Derived Fuel), the performance of 20 metallic and ceramic materials has been studied. Materials tested are Fe-based alloys, Fe/Ni-based alloys, Ni-based alloys, refractory and engineering ceramics. This paper reports the results for the alloys, while the refractories and ceramics are reported in reference [1]. They were regularly removed, examined and then put back into the gasifier. The metal degradation varies from 0.01 to 0.1 mm after three gasification campaigns. The gas composition was about 14% CO₂, 12% CO, 11% H₂O, 10% H₂, 4% CH₄, 2% C₂H₄, 300 ppm H₂S, 300 ppm HCl, bal. N₂. The corrosivity of the gas has been evaluated, concerning the potentials of oxygen, sulphur and chlorine. This gas characterisation has been made by calculating the potentials from the gas composition, and by examining the corrosion products on pure metals. Long time tests are running in a full scale power plant. Metallic and ceramic materials are being exposed for varying times in a biomass gasification atmosphere. Further, the environment in the gasifier is being characterized using pure metals.

1. Introduction.

This paper deals with metal corrosion studies during the use of gasification of refuse derived fuel (RDF). Metal and ceramic test pieces are being exposed in pilot scale as well as in full scale plant.

First some differences between the gasification process and combustion in general will be mentioned.

The ternary diagram in figure 1 shows the C-, H- and O-contents of some solid fuels [2].

The chars lie close to the carbon-corner. Coal contains a little more hydrogen and the biomass contains carbon, hydrogen and oxygen.

The diagram also shows that the analysis changes when the fuels are converted. After complete combustion the reaction products are represented by the line close to the oxygen corner between carbon dioxide and water.

“Gasification” can be defined as any process that shifts a fuel from the solid state to the gaseous state. In most cases that means a change in analysis into the area to the right of and above the CO/CH₄ - line.

The figure shows that the change in composition is much greater for coal gasifying than for biomass, which leads to higher energy output per ton of fuel.

The present interest in the gasification process is based on the inherently low emissions and the possibility to use a combined cycle.

The ternary C-H-O diagram, showed that the combustion reactions are obtained by com-

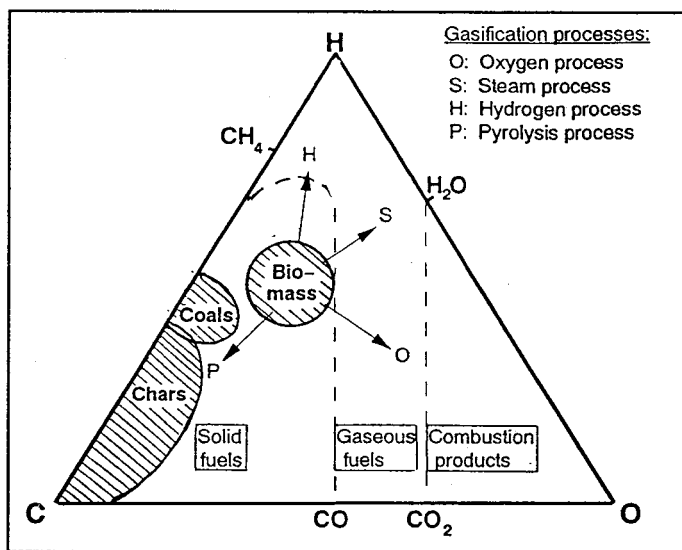


Fig. 1. — Coal conversion processes in relation to content of carbon, hydrogen and oxygen [1].

paratively high oxygen supply. Consequently, oxide layers are formed on the metal surfaces, and these layers often act as barriers for further attack from the gaseous environment.

However, combustion of waste leads to problems, due among other things to its chlorine content.

In spite of the dense oxide scales the chlorine manages to reach the metal and form gaseous or fluid metal chlorides or metal oxychlorides, which easily brake the scale.

During gasification of waste the situation is even worse.

In the reducing atmosphere with very low oxygen activity, the prerequisites for forming a stable oxide layer are limited.

Consequently, the detrimental components like sulphur and chlorine have better opportunity to attack the metal. As an example figure 2 shows the chlorine attack on chromium for different oxygen contents [3]. It can be seen that the metal degradation becomes catastrophic when there isn't sufficient oxygen to form a protective oxide layer.

In Studsvik, efforts are underway in two areas: primarily testing a number of materials in the waste gasification environment, secondarily characterizing that environment.

2. Exposing testpieces in pilot plant.

2.1 STUDSVIK CFBG ⁽¹⁾. — In Studsvik AB gasification processes have been studied and developed over the last decade. There is a 2 MWf CFBG⁽¹⁾ pilot plant, in which biomass and municipal and industrial waste are gasified.

The main part of the plant are shown in figure 3.

There are two fluidized beds: one FB where the fuel is gasified and one FB where the gas is cracked. In the cracker tar and ammonia in the gas are converted to non-condensable

⁽¹⁾ CFBG: Circulating Fluidized Bed Gasifier.

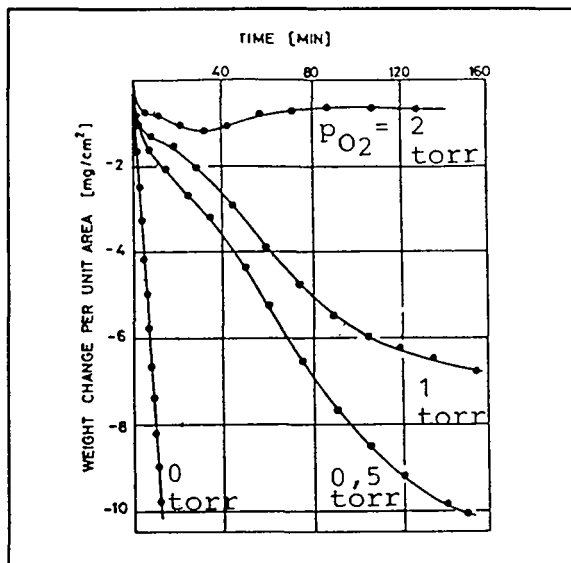


Fig. 2. — Chromium weight change for different oxygen pressures at chlorine partial pressure = 20 torr [2].

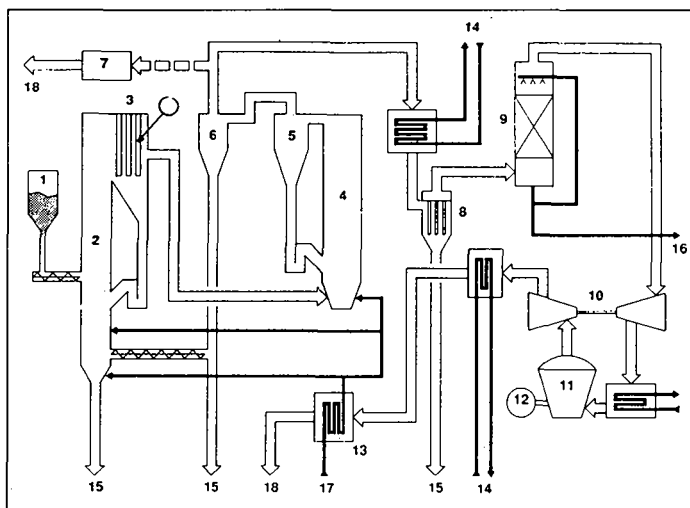


Fig. 3. — Studsvik CFBG pilot plant: 2) gasification chamber; 3) particle separators; 4) cracker.

gaseous components, such as carbon monoxide, hydrogen, nitrogen, methane. The cracker bed material is dolomite, which serves as a catalyst for the cracking reactions. The cleaned gas is burned in a diesel engine.

2.2 EXPOSURES. — During three waste fuel campaigns, about 200 hours in total, a number of metallic and ceramic test pieces have been mounted in the plant. Most of them are placed directly after the gasification chamber, where the most aggressive environment occurs. Certainly the sulphur and chlorine in the waste give high contents in the gas, about 0.1% each, which, in combination with low oxygen partial pressure, cause corrosive attack.

In all 31 pieces have been exposed, 17 of which are metallic and represent 11 different grades. After each campaign they were removed, examined and then remounted in the gasifier, and thus the intermediate results during the total exposure could be evaluated. Hitherto the pieces have been exposed during three campaigns for a total of about 200 hours.

The examination has included thickness measurement, surface layer measurement in a SEM, and for some pieces analysis of the elemental distribution in the surface.

2.3 RESULTS FROM THE EXPOSURE. — Figure 4 shows an example of the surface changes during the three campaigns. It is alloy 825, and the metal degradation after the campaigns increases to 0.05 mm, 0.07 mm and 0.09 mm, and, the penetrated layer grows to 0.03 mm, 0.07 mm and 0.1 mm respectively.

The metal degradation and penetrated layer for the other metals after three campaigns are shown in figure 5. The zero-line represents the original metal surface. The upper bar represents the thickness of the corrosion products formed on the surface, and the lower bar is the depth of internal penetration along the grain boundaries.

The figure shows that the total thickness of the corrosion products, for most of the grades varies between 0.1 and 0.2 mm, except the grade 253MA with a 1 mm coating of NiCrBSi which suffered a catastrophic degradation.

After these three short exposures it is not yet possible to draw any reliable conclusions and rank the grades for long time use. In sulphur free environments the nickel base grades are usually superior compared with the iron base grades. In this atmosphere, however, this isn't the case. Due to the sulphur in the gas an eutectum Ni-Ni₃S₂ is formed, with as low melting point as 635 °C. Thus the corrosion attacks are of the same order as for the iron base grades. The penetration layers are somewhat thicker.

The elemental distribution in the surface layer has been analysed in two samples.

The results from the nickel base grade HR160 (Fig. 6) show that chlorine is concentrated to the inner part of the surface layer, whilst the sulphur is distributed more evenly through the layer. In contrast, in the steel 253MA, the sulphur is concentrated to the innermost part of the penetration layer.

3. Gas characterizing.

So far this paper has dealt with the corrosion of metal and ceramic test pieces. However, the trials should also lead to increased knowledge of the environmental influences. This requires a characterization of the environment primarily with regard to an evaluation of the partial pressures of oxygen, sulphur and chlorine in the gas. These are very low, typical values for sulphur are 10⁻¹⁰ bar and for oxygen 10⁻²⁰ bar. Thus they cannot be accurately measured by conventional methods.

Other ways to evaluate the activities must be used. Figure 7 shows two principles for the characterisation of the gas.

An alloy is exposed to a corrosive gas with a certain composition. The corrosion products formed on the metal surface depend primarily on the activities of O, S and Cl, which unfortunately are too low to be measured directly.

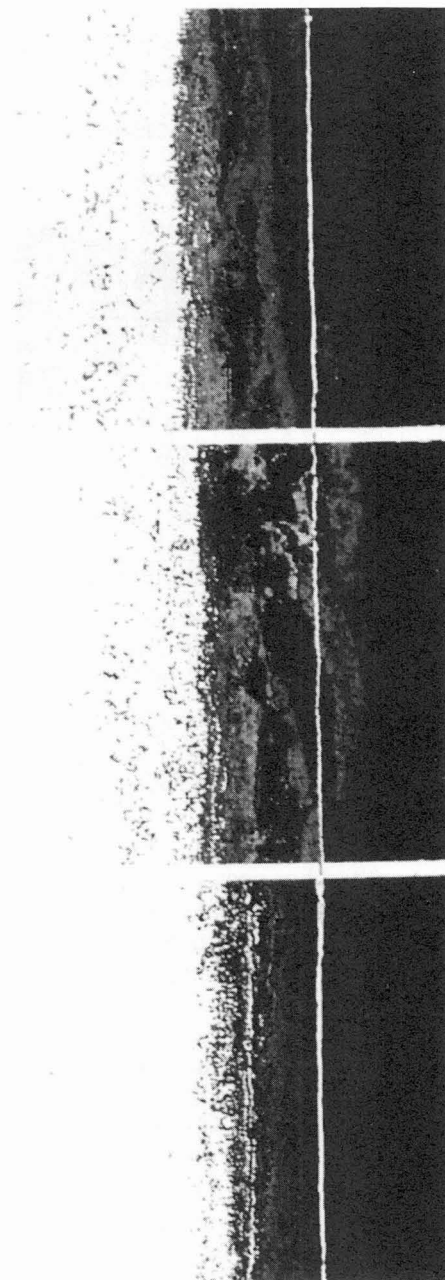


Fig. 4. — Microscope pictures after each campaign for inconel 825 (200 \times).

However, they can be evaluated from the gas composition by using thermodynamical equilibrium data. These calculated values represent the state when the gas reactions have reached equilibrium. Probably this is not the case in the real process.

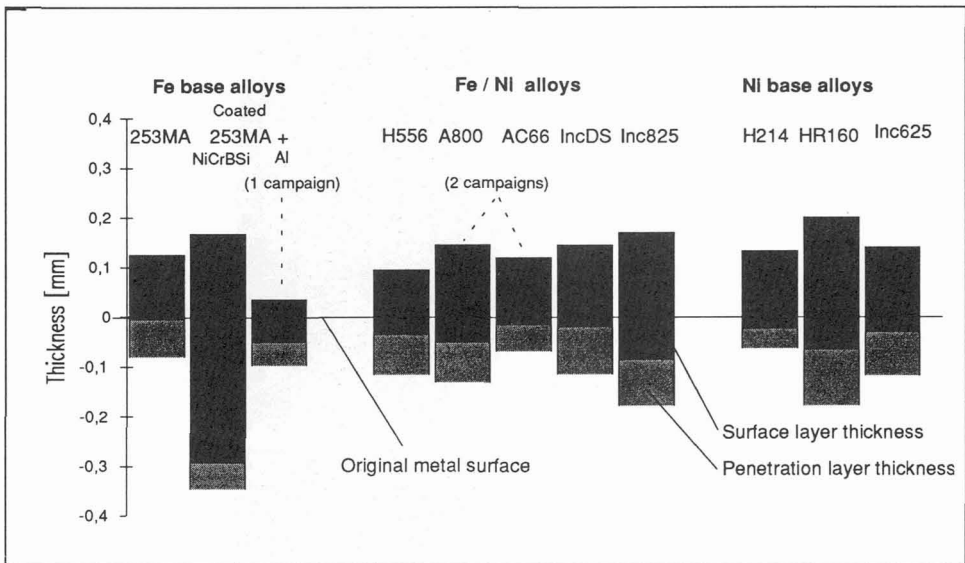


Fig. 5. — Results after three campaigns for all materials.

It is also possible to characterize the gas by going the opposite way. The corrosion products on pure, well defined elements can indicate which O and S activities the metal has been exposed to. Thus, by using a number of elements with various affinities to oxygen and sulphur we can find which “effective” activity of oxygen and sulphur there has been in the atmosphere. This value also includes the effect of surface, deposits, temperature and composition fluctuations and so on. The method has been developed by IAM⁽²⁾ Petten [4].

The calculation of the partial pressures of oxygen and sulphur is based on the measured gas composition, which is recalculated according to equilibrium conditions, including the partial pressures mentioned. The result plotted against the gas temperature is seen in figure 8, where the composition at 800 °C is marked.

In the figure the analysed gas composition is also indicated. Obviously that composition corresponds to the equilibrium composition at around 600 °C (with the exception of H₂). Probably this reflects the gas cooling, when the gas is sucked out before the analysis. At 800 °C the calculations give partial pressures for oxygen, sulphur and chlorine of 5×10^{-20} , 10^{-10} and 10^{-17} bars respectively.

The calculations represented in figure 8 assume carbon activity, $a_C = 0$. If that isn't the case the equilibrium changes. At $a_C = 1$ the oxygen partial pressure at 800 °C is 10^{-21} bar. The real circumstances lie somewhere in-between these two extremes.

The oxygen and sulphur partial pressures calculated are indicated in the thermodynamic phase diagram of figure 9.

This figure also shows the phases identified by X-ray diffraction analysis of the pure metal corrosion products⁽³⁾. The picture shows that many phases are found which shouldn't be there according to the calculated gas composition. The NiO and NiS identified show that the partial pressures of oxygen and sulphur have been considerably higher than calculated

⁽²⁾ IAM: Institute of Advanced Materials.

⁽³⁾ The analyses were performed by IAM, Petten

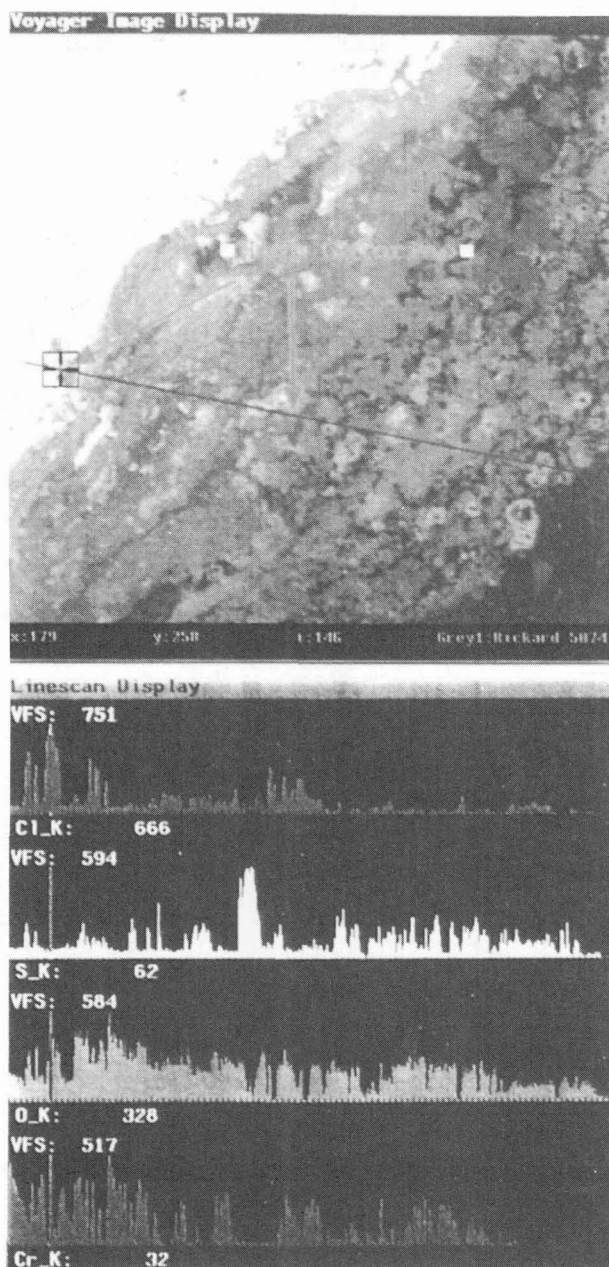


Fig. 6. — Distribution of Cl, S, O and Cr, analysed by Tracor Europe.

(above 10^{-14} and 10^{-9} bar respectively). Further, if the corrosion products of Pb (PbO and PbS), which were molten at the operation temperature, are considered the pressures have been even higher.

The divergence can be explained by intermittent operation of the pilot plant. The start-up

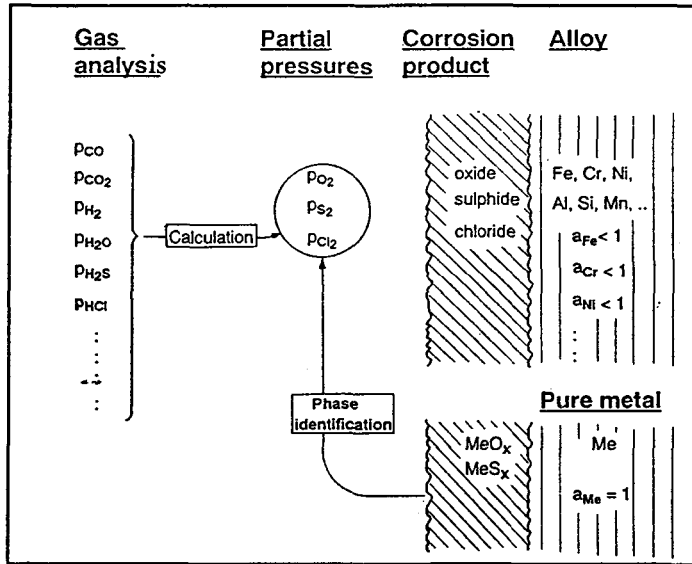


Fig. 7. — Gas characterizing.

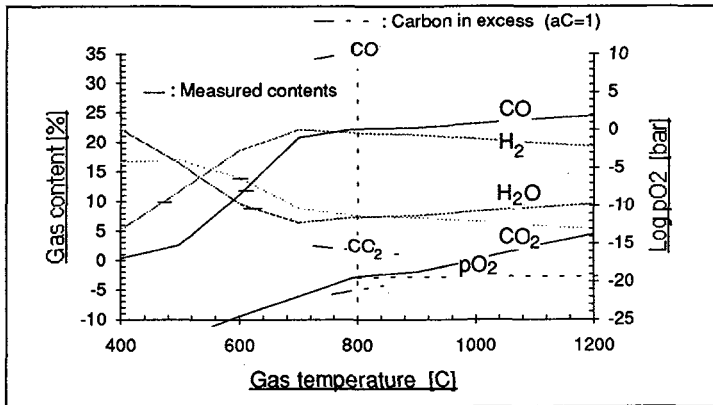


Fig. 8. — Gas composition versus temperature calculated with SOLGASMIX. Carbon activity ($a_C = 0$; Broken lines: $a_C = 1$).

and shut-down procedure during the campaigns, as well as some disturbances in the stable operation have caused air inlet on some occasions, leading to oxidation of the samples.

4. Exposing test pieces in a full scale plant.

The alloy performance tests as well as the experiments with pure metals, raise the question as to whether the tests under intermittent operation of the pilot plant are representative for materials in full scale service. In long term use the more stable temperature and environment

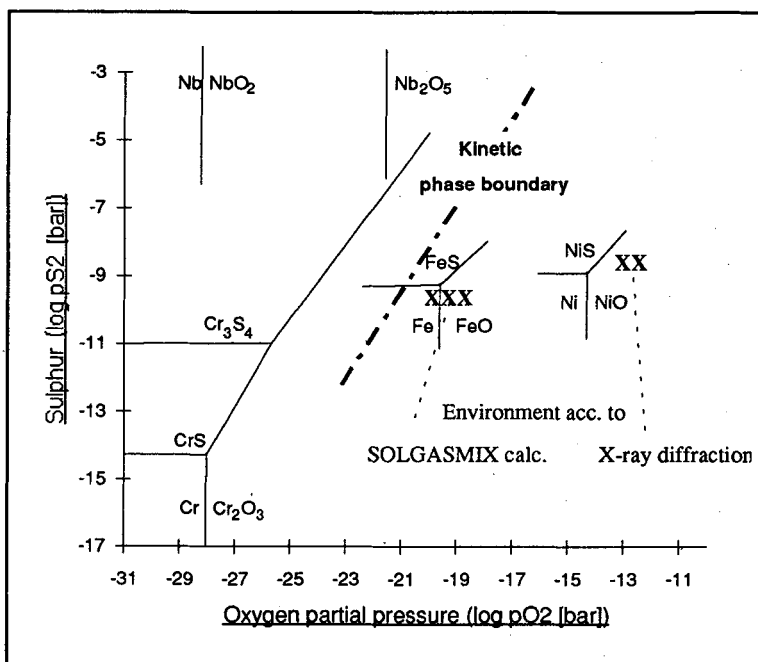


Fig. 9. — Thermochemical phase diagram with identified environments according to calculation respectively phase identification.

could result in corrosion layers on the surface which remain for a longer time.

Consequently long term tests are being made in a full scale waste gasifier of the Studsvik design. About 80 metallic, ceramic and pure metal test pieces are mounted in a rig, which is shown in figure 10.

At each maintenance stop the rig is lifted out. A set of 15 samples are taken away, each one representing one grade, whereupon the rig with the remaining samples is put back into the gasifier. This gives intermittent results over a period of one year or longer. The metal grades examined are shown in figure 11.

The gas is characterized by the pure metals method.

5. Conclusion and summary.

The activities at Studsvik Material AB concerning materials for gasification of refuse can be summarized as follows:

- Material performance tests during 200 h in a pilot plant show that surface layer and penetration layer thickness for the alloys are in the range of 0.02-0.2 mm each;
- Partial pressures in the gas were :
 - $p_{O_2} = 10^{-20} - 10^{-19}$ (bar),
 - $p_{S_2} = 10^{-10}$ (bar),
 - $p_{Cl_2} = 10^{-16}$ (bar);

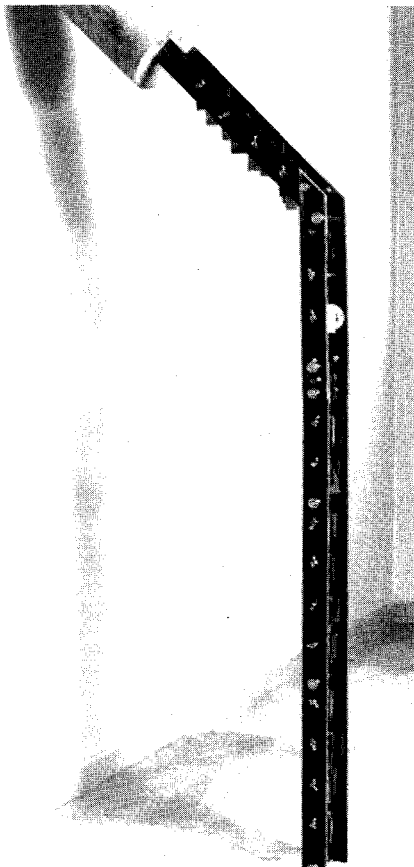


Fig. 10. — Test rig for exposure of metal and ceramic pieces in a full scale plant.

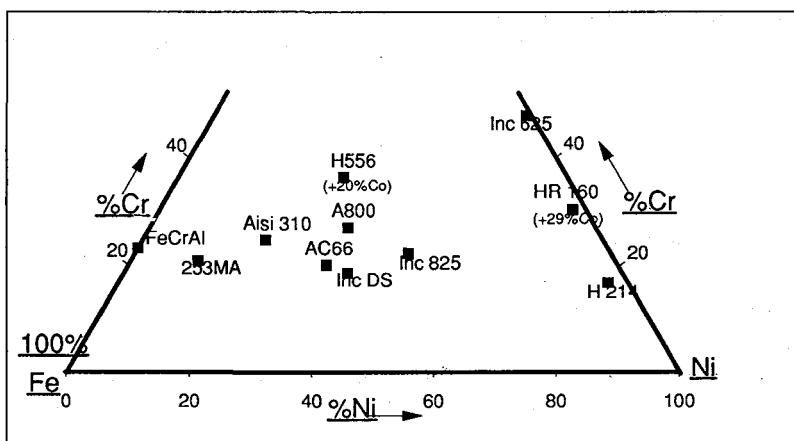


Fig. 11. — Tested metals in the full scale tests. See also table I.

Table I. — *Composition of tested HT-alloys.*

Material	Fe	Cr	Ni	Co	Others
FeCrAl	72	22			5Al, (Si)
253MA	68	21	11		0.17N, 0.08RE
Aisi310	55	25	20		
Hay556	27	27	20	20	3Mo, 3W, N, La, Zr, Cb, Ta
Alloy 800	40	27	32		0.4Al, 0.5Ti
353MA	39	25	35		1.4Si, 0.2Mo, 0.14N, 0.07Ce,
AC66	47	20	32		0.8Nb, 0.1Ce
Inc DS	43	18	35		2.5Si, 1Mn
Inc 825	31	21	42		3Mo, 2.25Cu, 0.9Ti
Haynes 214	3	16	76		5Al, Y
HR 160	2	28	62	29	2.8Si, 0.5Mo
Inc 625	1	48	51		0.35Ti

- Present and future activities:
 - Material performance tests in a full scale plant,
 - Gas characterization in a full scale plant.

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